Further Examination of the Reactions of Simple Indoles with Arenesulphonyl Azides

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3-Methylindole reacts readily in pyridine solution with *p*-chloro- and with *p*-nitro-benzenesulphonyl azides to give 1 : 2 reaction products; from the reactions between *p*-nitrobenzenesulphonyl azide and 3-methylindole in acetic acid solution a 1 : 1 reaction product has been isolated. Similar reactions of ethyl 1-methylindole-2-carboxylate yield ethyl 3-arylsulphonylaminoindole-2-carboxylates and these compounds, on hydrolysis and decarboxylation, give 3-arylsulphonylamino-1-methylindoles.

The properties of the product obtained by treating indole with tosyl azide can be adequately explained in terms of a tautomeric mixture of amino and imino forms of the former.

We have observed [1] that 3-methylindole reacts very slowly with tosyl azide in pyridine solution forming the 1 : 2 product (I; R = Me) in 25% yield. As *p*-chlorobenzenesulphonyl azide [2,3] and *p*-nitrobenzenesulphonyl azide [1] are more reactive than tosyl azide their reactions with 3-methylindole have been examined. The 1 : 2 products (I; R = Cl or NO_2) were isolated in good yields; and since the attack of the second molecule of azide is base-catalysed [1] we examined the reaction of 3-methylindole with *p*-nitrobenzenesulphonyl azide in boiling acetic acid; the 1 : 1 product (II) was obtained in 15% yield. This is the first 1 : 1 reaction product to be obtained from 3-methylindole and an arenesulphonyl azide. The i.r. spectrum (Nujol) of the material indicated that the compound was in the iminoindoline form, but the solid was insoluble in chloroform and in dimethyl sulphoxide and no n.m.r. spectrum could be obtained.

A solution of 2-*p*-tolylsulphonylaminoindole in dilute sodium hydroxide solution was methylated with dimethyl sulphate; from the alkali-insoluble material a monomethyl derivative (m.p. 147—149°) was isolated. The n.m.r. spectrum of the compound showed that it contained an *N*-methyl group (τ 6·82) and a proton at C-3; since it was not the known [2] 1-methyl-2-*p*-tolylsulphonylaminoindole (m.p. 200°) it must be the 2-*N*-methyl derivative (IIIa; R = H). The n.m.r. spectrum of compound (IIIa; R = H) in either $CDCl_3$ or $(CD_3)_2SO$ showed the compound to be entirely in the amino-form (IIIa). At the concentrations used we could have detected 2% of the tautomeric imino form (IIIb). This is in contrast to the properties of simple 2-aminoindoles.[4] Along with compound (IIIa; R = H) a second compound was formed which had an R_F value very close to that of (IIIa) and which was not isolated pure. The n.m.r. spectrum of the mixture showed that this second component was a dimethylated material containing one *C*-methyl group and one *N*-methyl group; the τ values for these signals were almost identical with those recorded [1] for the 3-Me and 2-*N*-Me groups in compound (IV; R = Me), indicating that the dimethylated compound had structure (IV; R = H). This conclusion was supported by the mass spectrum of the mixture.

When tryptamine was heated with *p*-chlorobenzenesulphonyl azide the only compound isolated was 3-[2-(*p*-chlorobenzenesulphonylamino)ethyl]indole, formed by

[1] A. S. Bailey, A. J. Buckley, and W. A. Warr, *J.C.S. Perkin I*, 1972, 1626.

[2] A. S. Bailey, A. J. Buckley, W. A. Warr, and J. J. Wedgwood, *J.C.S. Perkin I*, 1972, 2411.

[3] A. S. Bailey, A. J. Buckley, and J. F. Seager, *J.C.S. Perkin I*, 1973, in the press.

[4] R. J. Sundberg, 'The Chemistry of Indoles,' Academic Press, New York, 1970, p. 393; T. Hino, M. Nakagawa, T. Hashizume, N. Yamaji, Y. Miwa, K. Tsuneoka, and S. Akaboshi, *Tetrahedron*, 1971, **27**, 775.

the primary amino-group reacting with the $-SO_2N_3$ group.[5]

From the reaction of tosyl azide with 1-methylindole a small quantity of the 3-tosylamino-derivative (V; Z = Ts) has been isolated [2,6] and its structure proved by physical means; an alternative preparation of (V) has now been developed.[7] It was observed that ethyl indole-2-carboxylate and *p*-chlorobenzenesulphonyl azide gave a small yield (7%) of compound (VI; R^1 = H, R^2 = Cl). Since 1-methylindole reacts with azides more rapidly than indole, ethyl 1-methylindole-2-carboxylate was heated with tosyl, *p*-chlorobenzenesulphonyl, and *p*-nitrobenzenesulphonyl azides, giving the expected products (VI; R^1 = Me, R^2 = Me, Cl, or NO_2).

In the n.m.r. spectra of these compounds in deuteriochloroform the signal from one of the aromatic protons appears at much lower field than those from the other aromatic protons (see Table). This effect is not observed for solutions in dimethyl sulphoxide, and this signal is not observed in the spectrum of ethyl 1-methylindole-2-carboxylate. We suggest that in compound (VI) a strong hydrogen bond is formed between the NH and CO_2Et groups, thus forcing the oxygen atoms of the SO_2 group close to C(4)H as indicated; this hydrogen bond is broken in dimethyl sulphoxide solution. A similar situation exists in compound (VII),[8] the signal for C(4)H appearing at low field; the structure of (VII) has been confirmed [9] by *X*-ray crystallographic analysis. Methylation of compound (VI; $R^1 = R^2$ = Me) afforded the 3-*N*-methyl derivative (VIII) and in the n.m.r. spectrum of this compound the signal from C(4)H was not downfield from those of the other aromatic protons. The R_F values of compounds (VI; $R^1 = R^2$ = Me) and (VIII) were identical and the m.p. of the latter

(I) (II) (IIIa) (IIIb)

(IV) (VI) (VII)

(V) (VIII) (IXa) (IXb)

N.m.r. data

	Solvent *	NH	C(4)H † d	NCH_3	Protons *ortho* to SO_2 d	Aromatic m	CH_2 q	CH_3 t
(VI; $R^1 = R^2$ = Me)	C	2·09	1·82	6·13	2·49	2·5—3·0	5·86	8·71
	D	0·65		6·13		2·4—3·1	5·95	8·89
(VI; R^1 = Me, R^2 = Cl)	C	2·01	1·83	6·13	2·48	2·6—3·0	5·82	8·69
	D			6·11		2·3—3·1	5·84	8·78
(VI; R^1 = Me, $R^2 = NO_2$)	D	0·00		6·10	1·66	2·1—3·1	5·95	8·82
(VI; R^1 = H, R^2 = Cl)	C	1·5, 2·15	1·79		2·41	2·5—2·9	5·77	8·71
	D	−1·47, 0·78				2·6—3·4	6·24	9·12
(VII)	C		1·46	7·01	2·06	2·4—3·4		
	D		1·73	6·96	2·16	2·2—3·3		
(VIII) §	C			5·99	2·37	2·6—3·1	5·79	8·68

* C = $CDCl_3$, D = $(CD_3)_2SO$. † Broad doublets, *J* 8 Hz; *meta* coupling not resolved. § $TsN{\cdot}CH_3$ τ 6·63. Tosyl Me signals have been omitted.

[5] Houben-Weyl, 'Methoden der Organischen Chemie,' 1955, vol. 9, p. 654.

[6] R. E. Harmon, G. Wellman, and S. K. Gupta, *J. Heterocyclic Chem.*, 1972, **9**, 1191; *J. Org. Chem.*, 1973, **38**, 11.

[7] A. S. Bailey and A. J. Buckley, *Tetrahedron Letters*, 1972, 3949.

[8] A. S. Bailey, R. Scattergood, and W. A. Warr, *J. Chem. Soc.* (*C*), 1971, 2479.

[9] B. Denton and C. K. Prout, unpublished work.

was higher than that of the former. Hydrolysis of the esters (VI; R^1 = Me) yielded the corresponding carboxylic acids; when these acids (R^2 = Me or Cl) were heated to 170° they afforded compounds (V; Z = Ts or *p*-$ClC_6H_4{\cdot}SO_2$). At its m.p. the *p*-nitro-derivative gave an intractable tar.

Harmon has stated [6] that the n.m.r. spectrum of 2-*p*-tolylsulphonyliminoindoline (IX) 'could not be explained by assuming the presence of only the imino *A* and the amino *B* tautomers as reported by Bailey *et al.*,' with no further amplification. The difference between our data [2,10] and those of Harmon is a signal at 'τ 3·57 (s, shoulder)' (value in p.p.m.). The position of this peak, which is absent in our material, is very close to that of the 'water peak' in $(CD_3)_2SO$. Harmon prepared his samples in dioxan and isolated the material by precipitation with methanol and ether and the sample was not recrystallised. The reported values [11] for the chemical shift of the protons in dioxan are in the range δ 3·71—3·57 p.p.m. A sample containing 1 molecule of dioxan for every 20 molecules of (IX) could not be distinguished from pure (IX) by analytical data (Calc. for 20 $C_{15}H_{14}N_2O_2S,C_4H_8O_2$: C, 62·8; H, 5·0; N, 9·6; S, 11·0%. Calc. for $C_{15}H_{14}N_2O_2S$: C, 62·9; H, 4·9; N, 9·8; S, 11·2%). Yet in such a mixture the sharp signal of the dioxan protons would have approximately 14% of the intensity of the strongest singlet in the spectrum (tosyl CH_3) and 80% of the intensity of the signal of C(3)H in (IXb), since the equilibrium mixture contains 50% of form b. We have found traces of dioxan difficult to remove from some of our indole–azide reaction products. The n.m.r. spectrum of the sample of 2-*p*-methoxyphenylsulphonyliminoindoline [6] prepared in dioxan contained a signal at δ 3·53 p.p.m., but this signal is absent in the spectrum of the corresponding *p*-nitro-derivative [6] prepared in ethanol.

We have repeated our preparation of compound (IX), recrystallised it three times from acetic acid–propanol, dried it in high vacuum for 12 h at 110°, and re-determined the n.m.r. spectrum. The positions of the C(3)H signals (τ 4·25 and 5·90) were in good agreement with our reported [2] values and the intensity of the two signals as compared with the intensity of the CMe signal showed that all the protons at C-3 were accounted for by these signals. There was a small 'water peak' at τ 6·7. Although the addition of a 'drop' of water precipitates the material from solution we succeeded in adding 3 μl of water without precipitating the compound. The spectrum was unchanged apart from an increase in the size of the 'water peak.' To this solution was added 1 drop of trifluoracetic acid; the 'water peak' moved downfield to τ 2·7; the relative intensities of the signals at 4·25 and 5·90 remained unchanged and there was no sign of a signal between τ 6·0 and 7·2. The n.m.r. spectrum of (IX) was again recorded in $(CD_3)_2SO$ and then D_2O (3 μl) was added; after 10 min the spectrum was re-run. The intensities of the two signals at τ 4·23 and 5·90 had decreased by approximately 50%, showing that the C3 hydrogen atoms are exchanging and the solution we examined had reached equilibrium.

The n.m.r. spectrum has been run at four different temperatures. The proportions of the tautomers vary little with temperature and the indole is favoured at low temperatures: *K*{=[(IXb)]/[(IXa)]} 1·2 (20°), 1·09 (40°), 0·96 (60°), and 0·91 (80°). The value at 40° is close to that determined at 35° (1·08) earlier [2] for a different sample and with a different spectrometer.

Since we have been unable to detect any of the tautomer (IIIb) in compound (III) we believe that compound (IX) is well represented as a tautomeric mixture of forms a and b.

EXPERIMENTAL

Details of apparatus used have been published; [1-3] i.r. spectra are recorded for Nujol mulls (N) or solutions in chloroform (C); u.v. spectra are recorded for solutions in ethanol unless otherwise stated; n..m.r. spectra were determined for solutions in [^{2}H]chloroform unless stated otherwise.

3-(p-*Chlorophenylsulphonylamino*)-2-(p-*chlorophenylsulphonylimino*)-3-*methylindoline* (I; R = Cl).—A solution of 3-methylindole (1·3 g) and *p*-chlorobenzenesulphonyl azide (4·4 g) in pyridine (10 ml) was heated at 100° for 24 h. The pyridine was removed *in vacuo* and methanol (20 ml) was added to the residue. This was removed *in vacuo* and a second portion was added. Next day the solid was collected (4·5 g, 88%). Recrystallisation from 2-methoxyethanol gave *compound* (I; R = Cl) (4·1 g), m.p. 255—256° (Found: C, 49·2; H, 3·5; Cl, 13·6; N, 8·2; S, 12·3. $C_{21}H_{17}Cl_2N_3O_4S_2$ requires C, 49·4; H, 3·3; Cl, 13·9; N, 8·2; S, 12·5%); $\nu_{max.}$ (N) 1605br, 3230w, and 3270w cm^{-1}; $\lambda_{max.}$ ($CHCl_3$) 240, 273sh, 278, and 298 nm (ε 14,900, 9550, 9850, and 6650); τ [$(CD_3)_2SO$] 8·62 (3H, s, CMe), 1·9—3·5 (12H, m, Ar), 1·08 (1H, NH, exchanged D_2O), −1·27 (1H, NH, exchanged D_2O); *m/e* 509 (M^+, 15%), 334 ($M - ArSO_2$, 40%), 159 ($M - 2ArSO_2$, 100%). Similarly, 3-methylindole (1·3 g) and *p*-nitrobenzenesulphonyl azide (2·75 g) in pyridine (10 ml) (50°; 16 h) gave 3-*methyl*-3-(p-*nitrophenylsulphonylamino*)-2-(p-*nitrophenylsulphonylimino*)*indoline* (I; R = NO_2) (3 g). Recrystallisation from dimethylformamide–methanol (1 : 1) gave pale yellow needles (2·7 g), m.p. 217—220° (Found: C, 47·6; H, 3·4; N, 13·5; S, 12·2%; *M*, 531. $C_{21}H_{17}N_5O_8S_2$ requires C, 47·5; H, 3·2; N, 13·3; S, 12·1%; *M*, 531); $\nu_{max.}$ (N) 1537br, 1615, 1650br, 3245w, and 3325w cm^{-1}; $\lambda_{max.}$ 205, 263, and 290sh (ε 33,500, 28,500, and 15,300); τ [$(CD_3)_2SO$] 8·57 (CMe) and 1·5—3·5 (m, Ar); the compound was sparingly soluble and in the weak solution the broad NH signals could not be detected.

3-*Methyl*-2-(p-*nitrophenylsulphonylimino*)*indoline* (II).—3-Methylindole (1·3 g) and *p*-nitrobenzenesulphonyl azide (2·4 g) were dissolved in glacial acetic acid (20 ml) and heated (water-bath; 100°) for 2 days. The solvent was removed; the resulting tar was dissolved in the minimum of boiling methyl cyanide and an equal volume of methanol was added. Next day the solid (0·5 g) was collected. *Compound* (II) formed brown crystals, m.p. 228—230°

[10] A. S. Bailey, M. C. Churn, and J. J. Wedgwood, *Tetrahedron Letters*, 1968, 5953.

[11] L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' Pergamon, London, 1969, p. 200.

(Found: C, 54·3; H, 3·7; N, 12·5; S, 9·6. $C_{15}H_{13}N_3O_4S$ requires C, 54·4; H, 3·9; N, 12·7; S, 9·7%); $\nu_{max.}$ (N) 1537, 1610br,s, and 3340w cm^{-1}; $\lambda_{max.}$ 261 and 291sh nm (ε 15,900 and 8800).

2-(N-*Methyl-p-tolylsulphonylamino*)*indole* (III; R = H). —2-*p*-Tolylsulphonylaminoindole (2 g) [2] suspended in 2M-sodium hydroxide solution (40 ml) was warmed gently to 40°. To the clear solution was added water (20 ml), and the solution was cooled to room temperature. Dimethyl sulphate (0·6 ml) was added and the mixture was shaken vigorously; after 5 min more dimethyl sulphate (0·6 ml) was added, and then a final addition (0·8 ml) was made (total 2 ml; total time of shaking 30 min). The solid was collected, washed with dilute sodium hydroxide solution, ground under water, and again collected (700 mg). One recrystallisation from methanol gave a product (300 mg), m.p. 140—146°, which was shown (t.l.c. on silica in benzene–ethyl acetate, 9 : 1) to be mainly one compound. A second recrystallisation from methanol gave the *amide* as prisms (pure by t.l.c.), m.p. 147—149° (Found: C, 63·8; H, 5·3; N, 9·2%; *M*, 300. $C_{16}H_{16}N_2O_2S$ requires C, 64·0; H, 5·3; N, 9·3%; *M*, 300); $\nu_{max.}$ (C) 1540, 1580, 1598, 1620w, and 3450 cm^{-1}; $\lambda_{max.}$ 218, 273, 283, and 292 nm (ε 36,100, 8017, 8570, and 8310); τ 7·65 (3H, s, tosyl Me), 6·82 (3H, s, NCH_3Ts), 4·22 [1H, s, C(3)H], 2·5—3·0 (8H, m, Ar), 1·0 (1H, NH, exchanged D_2O); τ [$(CD_3)_2SO$] 7·65 (CMe), 6·85 (NMe), 4·10 [C(3)H], 2·45—3·10 (m, Ar), and −1·15 (NH). From the methanolic mother liquors the solid was isolated by evaporation; it was dissolved in benzene and light petroleum (b.p. 60—80°) was added. The solid which separated (240 mg) contained two components; the faster running (R_F 0·50) was (III; R = H) and a slower moving material, R_F 0·43, was present. The n.m.r. spectrum of the mixture showed the signals associated with (III; R = H) and those of a material giving signals at τ 8·35 [C(3)Me], 7·40, (tosyl Me), 6·71 (NCH_3Ts), and 1·9 (NH). The strengths of the signals indicate two parts of (III; R = H) to one of (IV; R = H). The mass spectrum of the mixture contained peaks at *m/e* 314 (IV; R = H) (14%), 300 (III; R = H) (30%), 159 (314 − Ts) (54%), and 145 (300 − Ts) (100%).

3-[2-(p-*Chlorophenylsulphonylamino*)*ethyl*]*indole*.— Tryptamine (1·6 g) and *p*-chlorobenzenesulphonyl azide (2·2 g) were dissolved in pyridine (10 ml). A vigorous reaction occurred and the temperature of the mixture rose to 40°. Next day the pyridine was removed and methanol was added; this was evaporated off and methanol (10 ml) was added to the residue. The solid (2·8 g) was collected and recrystallised from aqueous ethanol and then from ethanol–benzene giving the *amide*, white needles (2 g), m.p. 143° (Found: C, 57·9; H, 4·7; Cl, 10·7; N, 8·4; S, 9·8. $C_{16}H_{15}ClN_2O_2S$ requires C, 57·4; H, 4·5; Cl, 10·6; N, 8·3; S, 9·6%); $\nu_{max.}$ (N) 1592, 3260, and 3395 cm^{-1}; $\lambda_{max.}$ 223, 281, and 291 nm (ε 47,000, 5860, and 5050); τ 7·08 (2H, t, *J* 8 Hz), 6·93 (2H, t, *J* 8 Hz), 5·48 (1H, NH, exchanged D_2O), 2·5—3·1 (7H, m, Ar), 2·38 (2H, d, *J* 8 Hz, low-field half of $ArSO_2$ signal), and 1·97 (1H, NH, exchanged D_2O); *m/e* 333 (M^+, 9%) and 130 (C_9H_8N, 100%) (there were no other strong peaks).

Ethyl 3-(p-*Chlorophenylsulphonylamino*)*indole*-2-*carboxylate* (VI; R^1 = H, R^2 = Cl).—Ethyl indole-2-carboxylate (1·9 g) and *p*-chlorobenzenesulphonyl azide (2·2 g) were heated (100°) in pyridine (10 ml) for 2 days. The pyridine was removed and methanol (10 ml) was added. The solid which separated contained starting material and the mixture was chromatographed [silica (100 g); benzene–ethyl acetate mixtures]. The first fractions gave ethyl indole-2-carboxylate (0·6 g); later fractions yielded *compound* (VI; R^1 = H, R^2 = Cl) (0·25 g, 7%), which formed white needles, m.p. 209—211° (from ethanol) (Found: C, 53·9; H, 4·3; Cl, 9·1; N, 7·4; S, 8·4. $C_{17}H_{15}ClN_2O_4S$ requires C, 53·9; H, 4·7; Cl, 9·4; N, 7·4; S, 8·5%); $\nu_{max.}$ (N) 1556, 1583w, 1715s, 3270w, and 3445w cm^{-1}; $\lambda_{max.}$ 203, 229, and 300 nm (ε 18,900, 39,800, and 15,800); *m/e* 378 (M^+, 15%), 203 ($M - ArSO_2$, 100%), 157 (203 − C_2H_6O,[12] 29%), and 129 (157 − CO, 45%).

Ethyl 1-*Methyl*-3-(p-*tolylsulphonylamino*)*indole*-2-*carboxylate* (VI; R^1 = R^2 = Me).—Ethyl indole-2-carboxylate was methylated with dimethyl sulphate and sodium hydroxide in aqueous acetone, yielding ethyl 1-methylindole-2-carboxylate, m.p. 62° (75%) (lit.,[13] m.p. 63—64°); $\lambda_{max.}$ 207, 225, and 294 nm (ε 18,900, 23,600, and 18,900); τ 8·61 (3H, t, *J* 8 Hz), 5·94 (3H, s, NMe), 5·63 (2H, q, *J* 8 Hz), 2·4—3·0 (4H, m, Ar), and 2·30 (1H, d, *J* 8 Hz, Ar). The indole (1·9 g) and tosyl azide (2·1 g) were heated in pyridine (10 ml) at 100° for 2 days; the pyridine was removed and methanol (20 ml) was added. *Compound* (VI; R^1 = R^2 = Me) was collected and recrystallised from methanol. It formed white needles (1·0 g, 29%), m.p. 118—120° (Found: C, 61·2; H, 5·4; N, 7·7; S, 8·8. $C_{19}H_{20}N_2O_4S$ requires C, 61·3; H, 5·4; N, 7·5; S, 8·6%); $\nu_{max.}$ (N) 1554, 1586w, 1610w, 1627w, 1688s, and 3200 cm^{-1}; $\lambda_{max.}$ 228, 300, and 315sh nm (ε 28,000, 12,000, and 6000); *m/e* 372 (M^+, 16%) and 217 (M − Ts, 100%). Under the same conditions *p*-chlorobenzenesulphonyl azide yielded *ethyl* 3-(p-*chlorophenylsulphonylamino*)-1-*methylindole*-2-*carboxylate* (VI; R^1 = Me, R^2 = Cl), white needles (from ethanol), m.p. 135—137° (62%) (Found: C, 55·1; H, 4·3; Cl, 9·3; N, 7·1; S, 8·3. $C_{18}H_{17}ClN_2O_4S$ requires C, 55·0; H, 4·3; Cl, 9·1; N, 7·1; S, 8·2%); $\nu_{max.}$ (N) 1540, 1585w, 1677s, and 3260 cm^{-1}; $\nu_{max.}$ (C) 1713, 1681, 3348, and 3272 cm^{-1}; $\lambda_{max.}$ 230, 301sh, and 320 nm (ε 41,200, 16,100, and 6920); *m/e* 392 (M^+, 12%) and 217 ($M - ArSO_2$, 100%). The nitro-compound was prepared by heating the azide (6·2 g) and the indole (5·0 g) in pyridine (20 ml) at 65° for 1 day and then 100° for 1 day (yield 4 g). Recrystallisation from methyl cyanide gave *ethyl* 1-*methyl*-3-(p-*nitrophenylsulphonylamino*)*indole*-2-*carboxylate* (VI; R^1 = Me, R^2 = NO_2), yellow needles, m.p. 209—210° (Found: C, 57·6; H, 4·2; N, 10·4; S, 7·9. $C_{18}H_{17}N_3O_6S$ requires C, 57·7; H, 4·3; N, 10·4; S, 8·2%); $\nu_{max.}$ (N) 1528, 1602w, 1615w, 1692s, and 3300w cm^{-1}; $\lambda_{max.}$ ($CHCl_3$) 242, 304, 310sh, and 465 nm (ε 22,600, 14,200, 8800, and 900); *m/e* 403 (M^+, 9%) and 217 (100%).

1-*Methyl*-3-p-*tolylsulphonylaminoindole* (V; Z = Ts).— The ester (VI; R^1 = R^2 = Me) (0·5 g) was boiled in ethanol (10 ml) and 2M-sodium hydroxide solution (10 ml) for 10 min. A white solid separated. The mixture was acidified with hydrochloric acid and water (50 ml) was added. The solid was collected (0·45 g) and recrystallised from ethanol; the *acid* formed white crystals, m.p. 183—186° (decomp.) (Found: C, 59·4; H, 4·8; N, 8·3; S, 9·4. $C_{17}H_{16}N_2O_4S$ requires C, 59·3; H, 4·7; N, 8·1; S, 9·3%); $\nu_{max.}$ (N) 1543, 1610w, 1660br,s, 3265w, and 3350w cm^{-1}; $\lambda_{max.}$ 229, 300, and 320sh nm (ε 27,100, 10,700, and 4900); τ [$(CD_3)_2SO$]

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[13] J. R. Johnson, R. B. Hasbrouck, J. D. Dutcher, and W. F. Bruce, *J. Amer. Chem. Soc.*, 1945, **67**, 423.

7·67 (3H, s, tosyl Me), 6·12 (3H, s, NMe), and 2·3—3·0 (8H, m, Ar); *m/e* 344 (M^+, 0·3%) and 145 (M — Ts — CO_2, 100%). This acid was decarboxylated *in vacuo* (165°; 0·01 mmHg; 2 h); compound (V; Z = Ts) was isolated (86%), m.p. 183—184°, identical (t.l.c., n.m.r.) with the compound isolated previously.[2] Similarly, hydrolysis of the ester (VI; R^1 = Me, R^2 = Cl) yielded 3-p-*chlorophenylsulphonylamino*-1-*methylindole*-2-*carboxylic acid* (86%). Recrystallisation from ethanol gave white rhombs, m.p. 170—180° (decomp.) (Found: C, 52·6; H, 3·4; Cl, 10·0; N, 7·5; S, 8·9. $C_{16}H_{13}ClN_2O_4S$ requires C, 52·7; H, 3·7; Cl, 9·7; N, 7·7; S, 8·8%); $\nu_{max.}$ (N) 1525, 1580, 1650br,s, 3245, and 3280 cm^{-1}; $\lambda_{max.}$ 232, 300, and 315sh nm (ε 39,500, 13,100, and 6920); τ [$(CD_3)_2SO$] 6·11 (3H, s, NMe), and 2·3—3·0 (8H, m, Ar); *m/e* 364 (M^+, 0·4%), 320 (M — CO_2, 10%), and 145 (100%). The acid was decarboxylated under nitrogen at 190° (20 min) and the residue was recrystallised from chloroform yielding 3-p-*chlorophenylsulphonylamino*-1-*methylindole* (V; Z = *p*-$ClC_6H_4{\cdot}SO_2$) (50%), m.p. 185—186° (Found: C, 56·0; H, 4·2; Cl, 11·3; N, 8·6; S, 10·2. $C_{15}H_{13}ClN_2O_2S$ requires C, 56·2; H, 4·1; Cl, 11·1; N, 8·7; S, 10·0%); $\nu_{max.}$ (N) 1598, 1622w, and 3260 cm^{-1}; $\lambda_{max.}$ 222 and 285 nm (ε 36,700 and 6080); τ [$(CD_3)_2SO$] 6·30 (3H, s, NMe), 2·87 [1H, s, C(2)H], 2·6—3·2 (4H, m, Ar), 2·45 (2H, d, *J* 8 Hz, high-field half of $ArSO_2$ signal), and 2·27 (2H, d, *J* 8 Hz, low-field half of $ArSO_2$ signal); *m/e* 320 (M^+, 4%) and 145 (M — $ArSO_2$ 100%). Hydrolysis of the ester (VI; R^1 = Me, R^2 = NO_2) gave the corresponding *acid*, m.p. 175—180° (decomp.) (from aqueous ethanol) (yield 76%) (Found: C, 51·1; H, 3·5; N, 10·9; S, 8·5. $C_{16}H_{13}N_3O_6S$ requires C, 51·2; H, 3·5; N, 11·2; S, 8·5%); $\nu_{max.}$ (N) 1532s, 1610w, 1673br,s, 3927, and 3305sh cm^{-1}; $\lambda_{max.}$ 205, 233, and 296 nm (ε 26,700, 30,400, and 15,000); τ [$(CD_3)_2SO$] 6·09 (3H, s, NMe) and 1·6—3·0 (8H, m, Ar); *m/e* 331 (M — CO_2, 8%) and 145 (100%) (no M^+). Heating the acid to its m.p. gave an intractable tar.

Ethyl 1-*Methyl*-3-(N-*Methyl*-p-*tolylsulphonylamino*)*indole*-2-*carboxylate* (VIII).—Compound (VI; R^1 = R^2 = Me) (1·5 g) in acetone (100 ml) was methylated with dimethyl sulphate (3·3 ml) and sodium hydroxide (2·5 g) in water (10 ml). After 2 h the solution was poured into water and the product isolated by extraction (chloroform). The *ester* (VIII) (0·5 g) formed cubes, m.p. 129—130° (from methanol) (Found: C, 61·8; H, 5·8; N, 7·2; S, 8·4. $C_{20}H_{22}N_2O_4S$ requires C, 62·2; H, 5·7; N, 7·2; S, 8·3%); $\nu_{max.}$ (N) 1546w, 1602w, 1622w, and 1720s cm^{-1}; $\lambda_{max.}$ 226 and 298 nm (ε 34,700 and 16,600); *m/e* 386 (M^+, 8%), 231 (100%), and 185 (50%).

[3/375 *Received, 7th March,* 1973]